FINAl TECHNICAL REPORT

# Lasers for Studies of Quantum Dots and Molecules in Triplet States (DURIP)

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13. ABSTRACT (*Maximum 200 words*)

The final list of equipment purchased with DURIP plus matching funds is: 1. Innova Sabre DBW-15/3 Argon Ion Laser. 2. Upgrade 699-21 Dye Laser to 899-21 dye laser. 3. Upgrade 699-29 to Autoscan 899-29 Autoscan dye/Titanium Sapphire Laser. The Argon Ion Laser is being used in Professor Bawendi's studies of the optical and electronic properties of single semiconductor dots. The Autoscan titanium sapphire/dry laser (899-29) is beins used to study the structure and dynamics (mechanism of intersystem crossing) of triplet states of small polyatomic molecules. The 899-21 dry laser is being used in a collaborative project, to record dispersed fluorescence spectra of van der Waals molecules, with Prof W. Klemperer at Harvard University. One laser system has been used in conjunction with two single-quantum dot (or molecule) fluorescence detection systems that we have designed and built. In the past year we have studied the quantum confined Stark effect in nanocrystal quantum dots. We found that the electric field dependence of the signle-dot spectrum is characterized by a highly polarizable excited state, with the polarizabilty proportional to the volume of the dot.

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Equipment Acquired

In the original DURIP proposal, funds were requested for the purchase of the following lasers, all of which are from Coherent, Inc.:

1. Innova Sabre DBW-10/2 Argon Ion Laser
2. Innova Sabre R14 Argon Ion Laser
3. Upgrade 699-21 Dye Laser to 899-21
   Titanium Sapphire Laser ($1 cm^{-1}$ continuous single mode scan)
4. Upgrade #3 above from 899-21 to Autoscan 899-29
   ($300 cm^{-1}$ continuous single mode scan under computer control)

The original amount requested was $180,500 from DURIP plus $80,000 MIT nonfederal cost sharing: total $260,500. The amount provided by DURIP was reduced from the requested amount to $100,000 and the MIT cost sharing was therefore reduced to $60,000. As a result of the lower than initially requested funding level, item #2 was deleted from the equipment purchased. As the result of a substantial purchase of other laser equipment from Coherent, Inc. (as the result of an insurance reimbursement for the destruction of major equipment in Professor Field's laboratory), a substantial discount was negotiated. The final list of equipment purchased with DURIP plus matching funds is:

| | | |
|---|---|---|
| 1. | Innova Sabre DBW-15/3 Argon Ion Laser | $66,900.00 |
| 2. | Upgrade 699-21 Dye Laser to 899-21 dye laser | $44,000.00 |
| 3. | Upgrade 699-29 to Autoscan 899-29<br>Autoscan dye/Titanium Sapphire Laser | $68,484.53 |

For item #1, $60,000 was provided from MIT nonfederal cost sharing and $6,900 was provided from one of Professor Bawendi's grants. For item #2, $31,830 was provided from DURIP funds and $12,170 was provided from insurance reimbursement funds. For item #3, $68,484.53 was provided from DURIP funds.

Use of Equipment

The Argon Ion Laser is being used in Professor Bawendi's studies of the optical and electronic properties of single semiconductor quantum dots.

The Autoscan titanium sapphire/dye laser (899-29) is being used to study the structure and dynamics (mechanism of intersystem crossing) of triplet states of small polyatomic molecules.

The 899-21 dye laser is being used in a collaborative project, to record dispersed fluorescence spectra of van der Waals molecules, with Prof. W. Klemperer at Harvard University.

More details about each of these projects are provided below.

Objectives: No change from original proposal submitted 6 September 1996.

Status of Effort:

Lasers have been put into operation. Three lasers are involved. An Argon Ion laser is in use in Prof. Bawendi's laboratory, for use in spectroscopy of single quantum dots. An AUTOSCAN cw dye/Ti:sapphire laser (899-29 upgraded from 699-29) is in use in our AFOSR supported triplet project, to generate 0.003 $cm^{-1}$ spectral bandwidth tunable radiation for study of the doorway mediated intersystem crossing process in acetylene. A cw dye laser (899-21 upgraded from 699-21) is currently on loan to Professor William Klemperer at Harvard University. He is using this laser to record dispersed fluorescence spectra from Ar $I_2$ (excited via the $I_2\ B0_u^+ - X^1\Sigma_g^+$ chromophere) and ArHF (excited via the HF H—O vibrational overtone chromophore).

ACCOMPLISHMENTS/NEW FINDINGS

Single Quantum Dot Spectroscopy (Prof. Bawendi)

The laser system has been used in conjunction with two single-quantum dot (or molecule) fluorescence detection systems that we have designed and built. In the past year we have studied the quantum confined Stark effect in nanocrystal quantum dots. We found that the electric field dependence of the single-dot spectrum is characterized by a highly polarizable excited state, with the polarizability proportional to the volume of the dot. This polarizability is significantly higher than typical molecular values ($10^5$ cubic Angstroms compared to typical molecular values of 10 to 100 cubic Angstroms). Stark shifts in the lowest excited state more than two orders of magnitude larger than the linewidth were observed, suggesting the potential use of these nanocrystals in electro-optic modulation devices. We found that the Stark shifts also showed the presence of an induced dipole moment. This induced moment is the result of local random fields due to charges trapped at the interface between the dot and its surrounding. These charges move in time so that the induced dipole measured is constantly changing. In addition to giving rise to induced dipoles in the excited state of the dots, these local fields are also responsible for large spectral diffusion shifts observed both at 10 K and at room temperature. We have further investigated this spectral diffusion as a function of time, temperature, and light intensity, and we found that it is light driven. We also found that spectral diffusion is responsible for the linewidth in emission observed at room temperature. This is an important result because it means that if we can understand and control spectral diffusion, we may be able to slow it down and therefore narrow the emission linewidth of the dots at room temperature. We have recently added a Ti:sapphire system to our laser apparatus and are beginning to design a single dot fluorescence lifetime experiment. This experiment will address the question of the multiexponential decay observed in ensemble experiments. The question is whether each dot has a different lifetime, giving rise to the ensemble multiexponential lifetime, or whether the lifetime of each dot is itself multiexponential due to distributions of surface states, or to changes in the local environment.

Triplet Project (Prof. Field)

We are currently planning the pulse amplified cw Ti:sapphire part of the project. We have demonstrated that the signal to noise ratio in our Surface Electron Ejection Laser Induced Metastable (SEELEM) spectra improves rapidly as resolution is increased from 0.6 $cm^{-1}$ to 0.1 $cm^{-1}$. The present plan is to improve resolution from 0.1 $cm^{-1}$ to 0.003 $cm^{-1}$. This resolution improvement is essential to obtain spectra of sufficient quality to apply statistical pattern recognition methods to our SEELEM spectra. This will enable us to extract a level diagram which shows the crossing of the bright state ($S_1$) with a single doorway state ($T_3$), all embedded in a dense manifold of dark background states ($T_1$, $T_2$). Such a level diagram is central to elucidating the mechanism of intersystem crossing in acetylene.

Intracavity Dispersed Fluorescence from van der Waals Molecules (Prof. Klemperer)

The apparatus, consisting of a molecular beam which passes through the dye laser intracavity mode volume and a monochromator equipped with an array detector, has been put into operation. Initial spectra of $ArI_2$ will soon be recorded.

Personnel Supported

DURIP funds are not used for support of personnel. Personnel involved in the experiments utilizing the 899-29 dye/Ti:sapphire laser include:

| | | |
|---|---|---|
| Robert W. Field | (faculty, P.I.) | |
| J. I. Steinfeld | (faculty) | Remote Sensing |
| Stephen Drucker | (postdoc) | Triplets |
| Kevin Cunningham | (graduate student) | Triplets |
| Selen Altunata | (graduate student) | Triplets |
| Ilia Dubinsky | (graduate student) | Triplets |
| Michelle Silva | (graduate student) | Remote Sensing |

Personnel involved in the experiments at Harvard University utilizing the 899-21 dye laser include:

| | | |
|---|---|---|
| William Klemperer | (faculty) | van der Waals DF |
| Amy Miller | (postdoc) | van der Waals DF |
| Cheng-Chi | (graduate student) | van der Waals DF |

Personnel involved in the experiments utilizing the Argon Ion Laser include:

| | | |
|---|---|---|
| Moungi Bawendi | (faculty, co-PI) | Quantum Dots |
| Stephen Empedocles | (graduate student) | single quantum dots |
| Robert Neuhauser | (postdoc) | single quantum dots |
| Kentaro Shimizu | (graduate student) | single quantum dots |
| Masaru Kuno | (graduate student) | MCD |
| Catherine Leatherdale | (graduate student) | Photovoltaics |
| Mark Kastner | (faculty) | Q. D. Photoconductor |
| Michael Rubner | (faculty) | Thin Film Photovoltaics |

Publications:

1. Quantum-Confined Stark Effect in Single CdSe Nanocrystallite Quantum Dots, S. A. Empedocles and M. G. Bawendi, Science 278, 2114-2117 (1997).

2. Magnetic Circular Dichroism study of CdSe Quantum Dots, M. Kuno, M. Nirmal, M. G. Bawendi, Al. Efros, and M. Rosen, J. Chem. Phys. 108, 4242 (1998).

3. Influence of Spectral Diffusion on the Lineshapes of Single CdSe Nanocrystallite Quantum Dots, S. A. Empedocles and M. G. Bawendi, Submitted.

4. Polarization Spectroscopy of Single CdSe Nanocrystallite Quantum Dots, S. A. Empedocles, R. Neuhauser, and M. G. Bawendi, in preparation.

Interactions/Transitions

The project to record dispersed fluorescence spectra of van der Waals molecules is an MIT-Harvard Collaboration. The quantum dot photoconduction experiments are in collaboration with Prof. Mark Kastner of the MIT Department of Physics. The triplet project began as an MIT-UCSB collaboration (Prof. Alec Wodtke).

New Discoveries, Inventions, Patents

None

Honors:

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|---|---|
| Robert W. Field | William F. Meggers Prize, Optical Society of America, 22 October 1996<br>Doctor of Science (Honoris Causa), Amherst College, 24 May 1997<br>Fellow, American Academy of Arts and Sciences, 5 October 1998 |
| Moungi G. Bawendi | Nobel Laureate Signature Award, ACS, April, 1998<br>School of Science Graduate Teaching Award, MIT, May 1998<br>Coblentz Prize for Molecular Spectroscopy, June 1997 |